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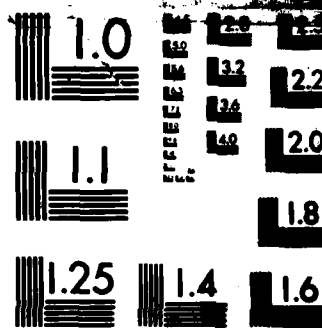
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SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL
INFORMATION STORAGE.
SOLID-STATE ELECTROCHROMIC CELL USING LUTECIUM DIPHthalOCYANINE

By

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solid-state electrochromic cells of the general configuration <table border="1"> <tr> <td>Lutecium Diphthalocyanine</td> <td>poly(Amps)</td> <td>Nafion</td> <td>poly(Amps)</td> <td>SnO₂</td> </tr> <tr> <td>on SnO₂ Cond. glass</td> <td>+ SE</td> <td>117</td> <td>+ CeCl₃</td> <td>Cond. glass</td> </tr> </table> <p>Were prepared using the supporting electrolytes (SEs) 0.1M Na₂SO₄ and 0.1M KCl. Upon subjecting the cell to anodic and cathodic voltage scans, up to four distinct color changes were observed varying from red (at anodic potentials) to violet (at cathodic potentials). Formation of the violet lutecium diphthalocyanine reduction product was not found contingent upon the absence of alkali cations as reported by others.</p>				Lutecium Diphthalocyanine	poly(Amps)	Nafion	poly(Amps)	SnO ₂	on SnO ₂ Cond. glass	+ SE	117	+ CeCl ₃	Cond. glass
Lutecium Diphthalocyanine	poly(Amps)	Nafion	poly(Amps)	SnO ₂									
on SnO ₂ Cond. glass	+ SE	117	+ CeCl ₃	Cond. glass									

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Absorbance spectra for lutecium diphthalocyanine in chloroform using a spectrophotometer.

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2.

CV for the electrochromic cell:

SnO_2	LuH(Pc)_2	Poly(Ampe)	Nafion 117	Poly(Ampe)	SnO_2
Cond. Glass		$0.1\text{M}^+ \text{Na}_2\text{SO}_4$		$0.1\text{M}^+ \text{Na}_2\text{SO}_4$	Cond. glass

$0.04\text{M} \text{CaCl}_2$

Sweep rate: 15 mv/sec.

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3.

CV for the electrochromic cell:

SnO_2	LuH(Pc)_2	Poly(Ampe)	Nafion	Poly(Ampe)	SnO_2
Cond. Glass		$0.1\text{M} \text{KCl}$	117	$0.1\text{M} \text{KCl}$	Cond. Glass

$0.04\text{M} \text{CaCl}_2$

Scan Rate: 20 mV/sec.

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EXPERIMENTAL

Lutecium Diphthalocyanine was prepared by direct solid-state reaction between lutecium acetate and o-phthalonitrile (alpha) by heating under Ar at 300°C for two hours. The reaction product was isolated from the reaction mixture using chloroform followed by a careful washing with organic solvents (acetic anhydride, methanol and acetone) for the removal of trace impurities. Evaporation of the lutecium diphthalocyanine was performed onto SnO₂ conducting glass (PPG Industries) using an Edwards 300A thin-film evaporator at 10⁻⁵ torr. Electrochemical measurements were performed using either a Stonehart Associates BC 1200 or a Wenking LT 78 potentiostat controlled by a BAS Model CV-1B cyclic voltammetry unit. Current-voltage data were recorded on a Houston Instruments Omnigraphic Model 154-046 X-Y recorder. Lutecium diphthalocyanine pellets were pressed in a KBr die using a Carver Hydraulic Press. Current collection to the SnO₂ conducting glass slide was performed by use of a nichrome wire attached via the use of silver epoxy (Epoxy Technology, Inc.) followed by curing at 150°C for one hour. Absorption spectra measurements were performed using a Bausch and Lomb Spectronic 21 Spectrophotometer.

RESULTS AND DISCUSSION

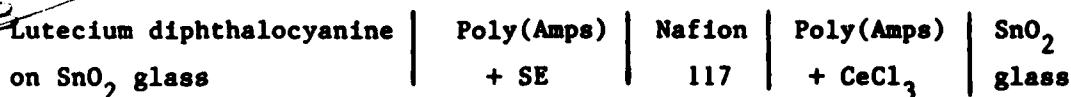
The overall program goal is to perform a basic investigation of photoelectrochemical and electrochemical effects by electrochromic materials in solid polymer electrolyte (SPE) containing solid-state cells. Initial investigations have been directed towards reversible electrochromic behavior at the interface between lutecium diphthalocyanine deposited onto electronically conducting glass, and the homopolymer poly-2-acrylamido -2-methylpropane sulfonic acid (poly(Amps)).

The presence of electrochromic effects on rare earth diphthalocyanine thin films after their deposition onto suitably conducting substrates was first reported by Russian workers^{1,2}, using aqueous KCl electrolytes. Greatest interest has been on lutecium diphthalocyanine ($\text{LuH}(\text{Pc})_2$) where Pc signifies the $\text{C}_{32}\text{H}_{12}\text{N}_8^{2-}$ group. This material, after deposition, possesses an initial green color (reported absorption peak 660.5nm^3) which upon potentiostating either anodic or cathodic of its initial rest potential in aqueous electrolyte can be made to undergo four or five distinct and reversible color changes. For example, passage of an anodic current through this electrochromic material will lead to the formation of a red oxidation product whereas passage of a cathodic current can lead to either blue or violet reduced materials, apparently dependent upon the nature of the supporting electrolyte.

Extensive work has been performed to date on delineating the nature of those lutecium diphthalocyanine species responsible for these color changes upon the passage of either anodic^{4,5} or cathodic⁶ currents while in contact with aqueous electrolyte. These latter studies were performed using $\text{LuH}(\text{Pc})_2$ thin films deposited onto an alumina substrate partially immersed in the aqueous electrolyte of interest. Here the reaction front could be monitored by the color change occurring along the moving boundary as in thin layer chromatography (TLC) techniques. The incentives for investigating this technology area lies in its eventual utility in multi-color flat-panel displays which are readable under bright ambient illumination. There would be obvious advantages in substituting aqueous by solid polymer electrolytes in such devices.

We wish to report here some recent work on solid-state electrochromic cells in which ionic mediation to thin-film deposits of lutecium diphthalocyanine is via the homopolymer poly-2-acrylamido-2-methyl propane sulfonic acid

cont'd
 (poly-Amps). Separation between the working (LuH(Pc)_2) deposited onto SnO_2 conducting glass) and counter (CeCl_3 in poly(Amps)) electrodes in these solid-state cells was realized by the use of the insoluble copolymer perfluorosulfonic acid (Nafion). The overall solid-state cell configuration used in this study can be represented by:



where the supporting electrolyte (SE) used in both working and counter electrode compartments was either 0.1M Na_2SO_4 or 0.1M KCl.

Lutecium diphthalocyanine was prepared by direct solid-state reaction between lutecium acetate and o-phthalonitrile (Alfa) using procedures previously documented by others². The isolated green reaction product was initially pressed into small pellets using a KBr die to facilitate material retainment within the evaporation boat during thin-film evaporation of this material. The absorption spectra of the LuH(Pc)_2 obtained after dissolution in chloroform is shown in Figure 1 using a spectrophotometer. A major peak occurred at 630nm with a minor shoulder present at 710nm. Other workers³ have reported this major peak being located at 660.5nm. LuH(Pc)_2 was evaporated (using an Edwards 306A thin-film evaporator) at 10^{-5} torr onto an SnO_2 conducting glass electrode. This resulted in a pale green film being deposited possessing a thickness of 2600Å. This deposition thickness was estimated based on the amount of charge that had to be passed through the solid-state cell to affect a given color change.

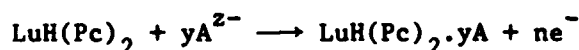
Solid-state cells were prepared by applying a thin-film (≈ 2 microns) of poly(Amps) (obtained as a 10^{-4} solution in water from Aldrich) containing either 0.1M KCl or 0.1M Na_2SO_4 as a supporting electrolyte, onto the deposited LuH(Pc)_2 film. After permitting the polymer to initially dry in the atmosphere for one hour, this electrode was directly contacted to the proton conducting Nafion 117 membrane. The counter electrode compartment consisted of a similar poly(Amps) film placed between the Nafion membrane and the SnO_2 conducting glass slide with redox electrochemistry being maintained upon cell cycling by the presence of 0.04M CeCl_3 . After pressing both of these half-cells together, the resultant solid-state cell was permitted to dry a further 30 minutes before initiating any electrochemical measurements.

Cyclic voltammetry (CV) measurements on the prepared cell possessing

Na_2SO_4 as the supporting electrolyte, are shown in Figure 2 using a sweep rate of 15mV/s. The logistics associated with these thin solid-state cells inhibited the use of a reference electrode. Consequently, working electrode potentials are recorded as a function of the larger counter electrode. Initial cathodic scan resulted in the LuH(Pc)_2 film becoming bright blue at -1.5V vs. SnO_2 glass with no further color change occurring at more negative potentials. Subsequent anodic potential scan resulted in the reappearance of the initial LuH(Pc)_2 green color as represented by the oxidation peak at 0.6V. The film became red at 1.3V. These color changes were found quite reversible upon repeated anodic and cathodic voltage scanning. Upon cathodic scan from 1.6V to -1.6V, the lutecium compound changed color directly from red to blue without the intermediate green. This color only appeared upon anodic scan from the reduced blue material.

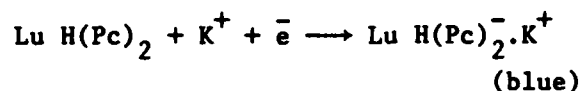
For solid-state cells prepared using 0.1M KCl as the supporting electrolyte, a representative CV is shown in Figure 3 using a scan rate of 20mV/s. Upon cathodic scan, the initial green LuH(Pc)_2 became blue (at -0.8V) and then violet (at -1.3V). Reversing scan direction returned the blue color at 1.1V, green at 1.0V and red at 1.5V. In comparison to cells using Na_2SO_4 as the supporting electrolyte, the KCl containing polymer returned the initial green LuH(Pc)_2 species upon cathodic scan from the oxidized red species formed at 1.5V. Additionally, the presence of KCl promoted formation of the violet reduced species at -1.3V. Again, these color changes were quite distinct and electrochemically reversible upon repeated cycling.

It has been suggested by others⁴ investigating electrochromic effects in KCl or Na_2SO_4 containing aqueous electrolytes that the anodic process can be represented by the general reaction:

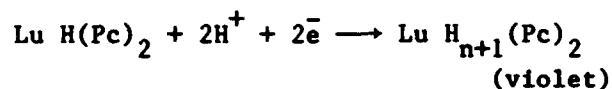


where A^{z-} represents the mobile anions Cl^- or SO_4^{2-} . Initial results have suggested that the red oxidation product may be a solid anionic conductor⁴ possessing (in Cl^- containing solutions) a mobility of $4 \times 10^{-6} \text{ cm}^2/\text{V} \cdot \text{sec}$, although the presence of mixed ionic/electronic conductivity might be anticipated for such materials.

The cathodic electrochromic reaction leading to the formation of blue and violet products has been suggested⁶ to occur by the following reactions:



and when an adequate supply of protons is available in the electrolyte



The violet reduction product has been estimated to possess a charge carrier mobility of $8 \times 10^{-7} \text{ cm}^2/\text{Vsec}$.

These results show that the observed electrochromic effect in these solid-state SPE cells has some dependency upon the supporting electrolyte incorporated within the homopolymer. We have not found, however, that formation of the violet reduction product is contingent upon the absence of alkali cations as reported by others⁶.

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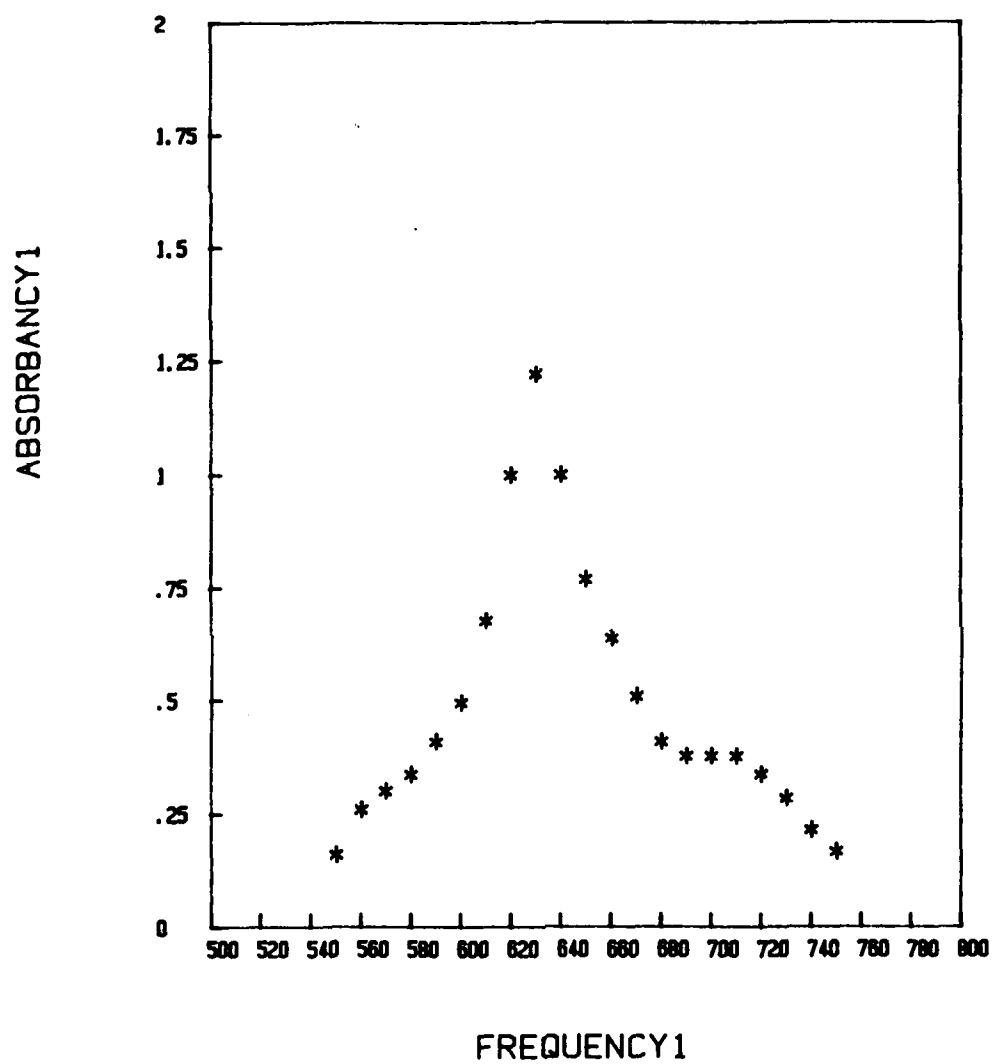
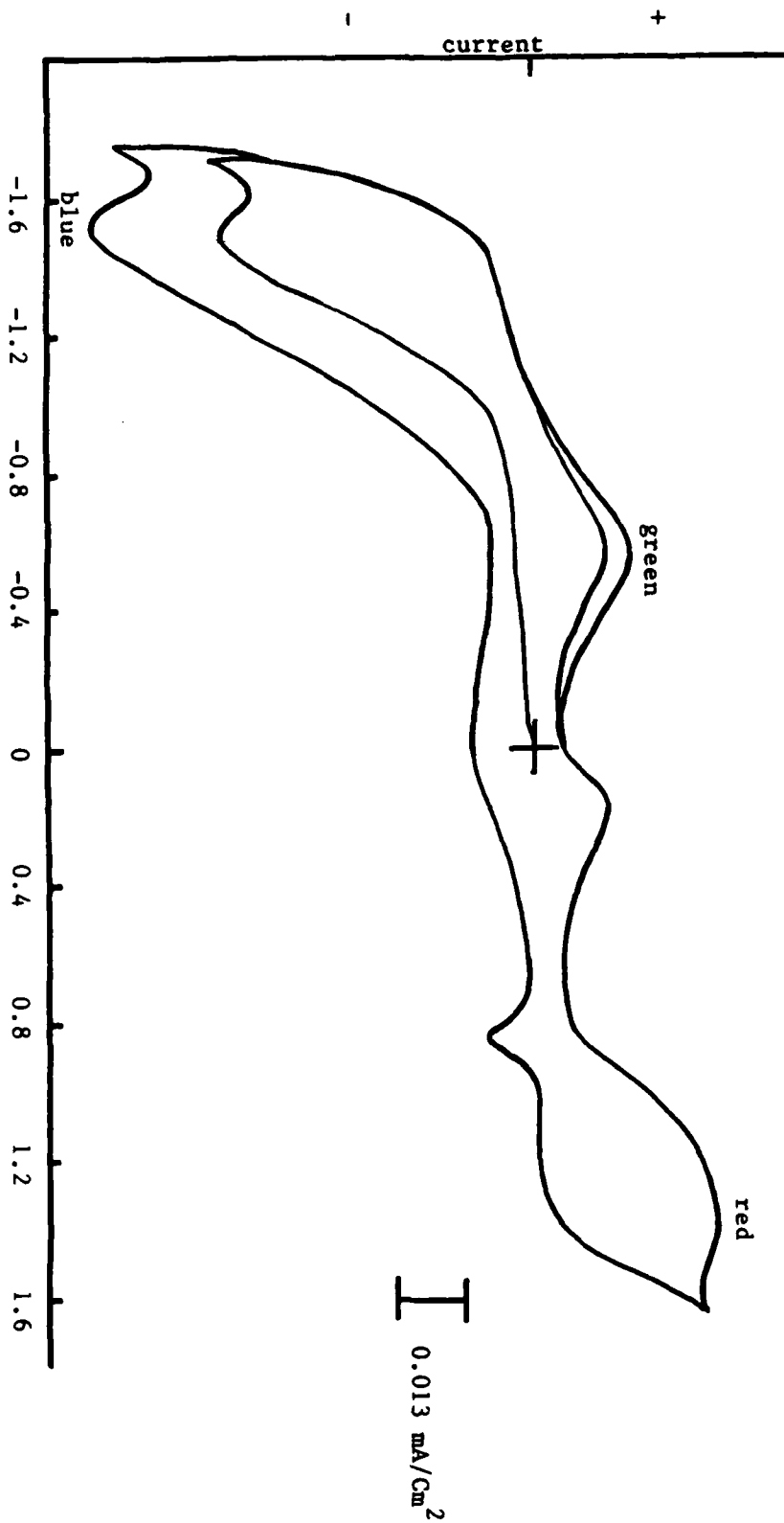


Figure 1. Absorbance spectra for lutecium diphthalocyanine in chloroform using a spectrophotometer.



Electrode potential vs. SnO_2 conducting glass reference/counter electrode (volts)

Figure 2. CV for the electrochromic cell:

SnO_2		LuH(Pc)_2		Poly(Amps)		Nafion 117		Poly(Amps)		SnO_2
Cond. Glass				$0.1\text{M } \text{Na}_2\text{SO}_4$				$0.1\text{M } \text{Na}_2\text{SO}_4$		Cond. glass
								$+$		
								$0.04\text{M } \text{CeCl}_3$		

Sweep rate: 15 mV/sec.

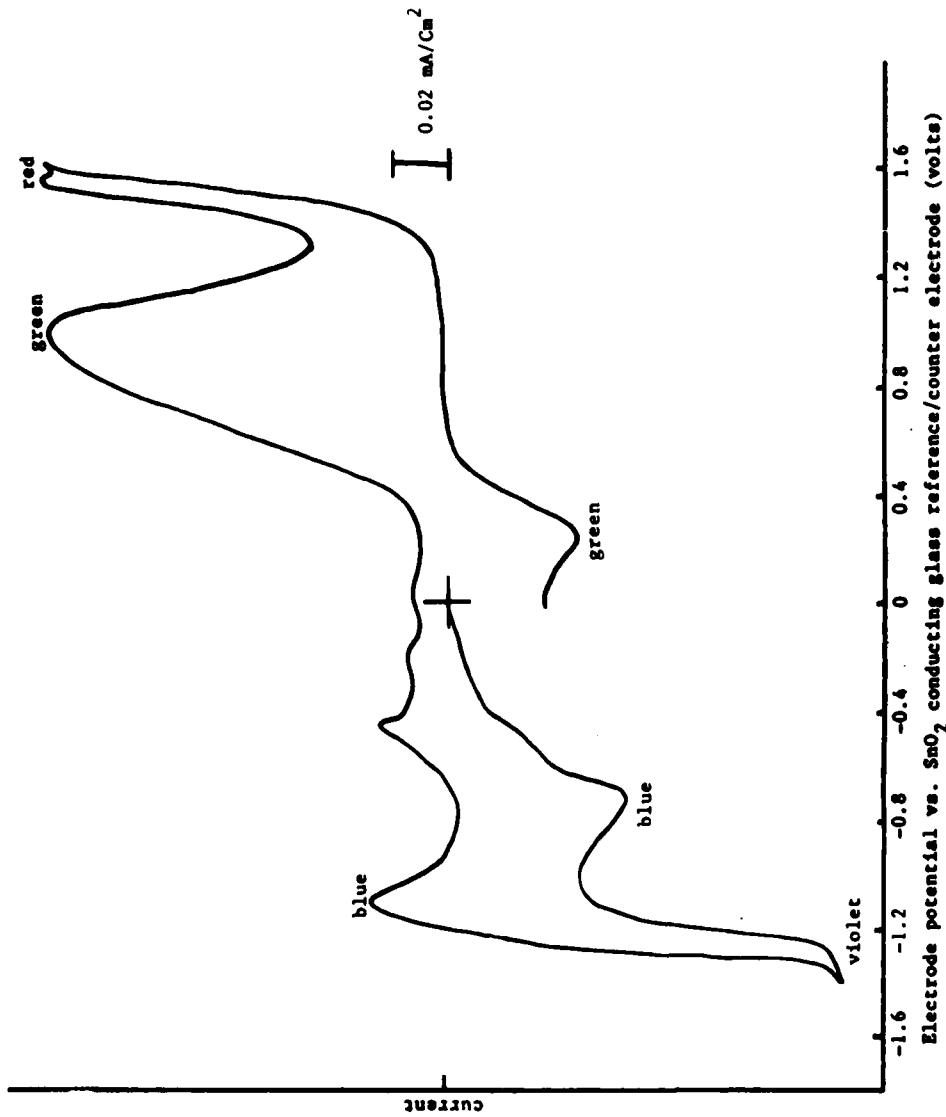


Figure 3. CV for the electrochromic cell:

SnO ₂	LuH(Pc) ₂	Poly(Amps)	Nafion	Poly(Amps)	SnO ₂
Cond. Glass		+ 0.1M KCl	117	+ 0.1M KCl	Cond. Glass
				+ 0.04M CeCl ₃	

Scan Rate: 20 mV/sec.

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